Multiplexed Sensor for Synthesis Gas Composition and Temperature

DOE University Coal Research Project
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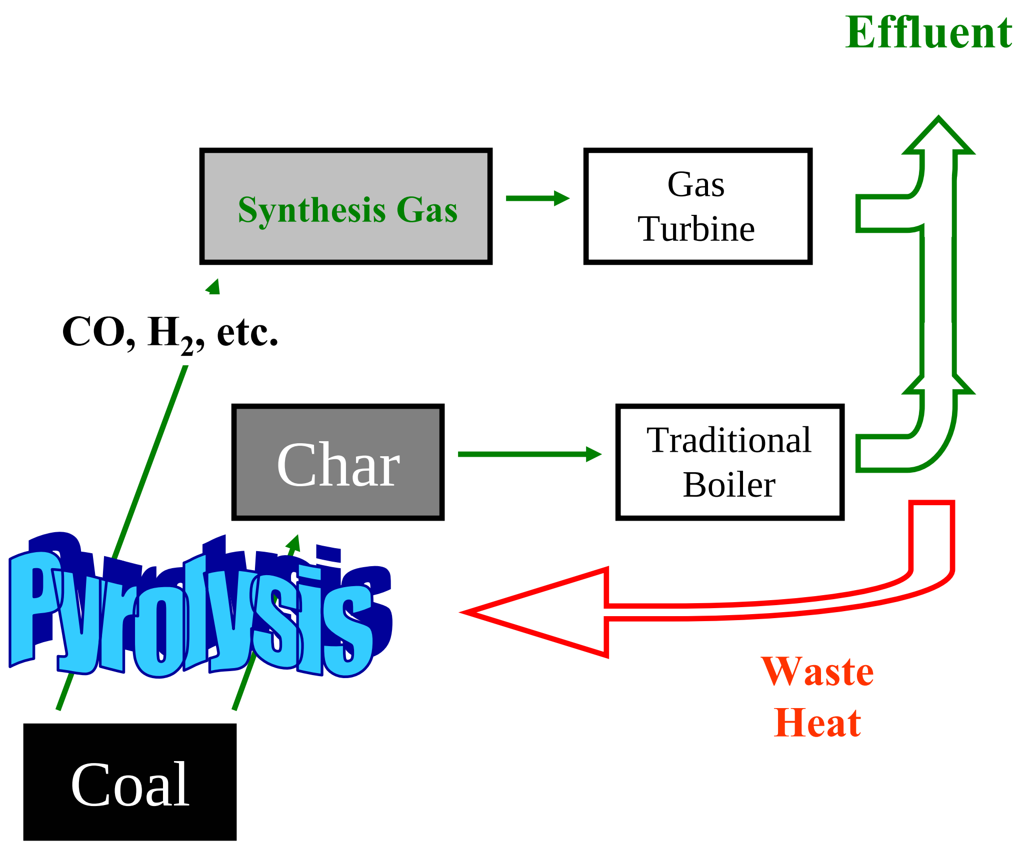
UCSD Jacobs | Mechanical and Aerospace Engineering

Outline of talk

- Introduction and motivation
- Abbreviated description of the sensing technique
- Sensor design
- Development of new spectroscopy
- Progress on measurements
- Upcoming work

The promise of gasification

- "Baseline" coal plants are ~ 33-35% thermal efficiency
- Integrated combined-cycle plants may exceed 50% thermal efficiency
- May aid in CO_2 sequestration
- Fischer-Tropsch fuels from syngas



The goals of this project

- **Integrated high-speed sensor that can measure composition of important major and minor species in real time and *in situ*.**
- ***Targeted species*: CH_4, H_2O, CO, CO_2, NH_3, H_2S**

➔ **Challenges**

- High, variable temperature
- High, variable pressure
- Sensitivity with short pathlength
- Rugged design

Benefits to tunable diode laser approach

- **Near-infrared tunable diode lasers have been developed by large telecommunications investment**
  - Relatively inexpensive hardware
  - Durable hardware
- **Direct optical measurements are obtained in real-time without perturbations to concentrations that might occur in a sampling system**
- **Measurements can easily be performed at several hundred Hz**
- **Laser light can be multiplexed and fiber-coupled**
- **Multiple species can be simultaneously measured with one detection system**

Familiar ground: Absorption spectroscopy

- **Beer's law**

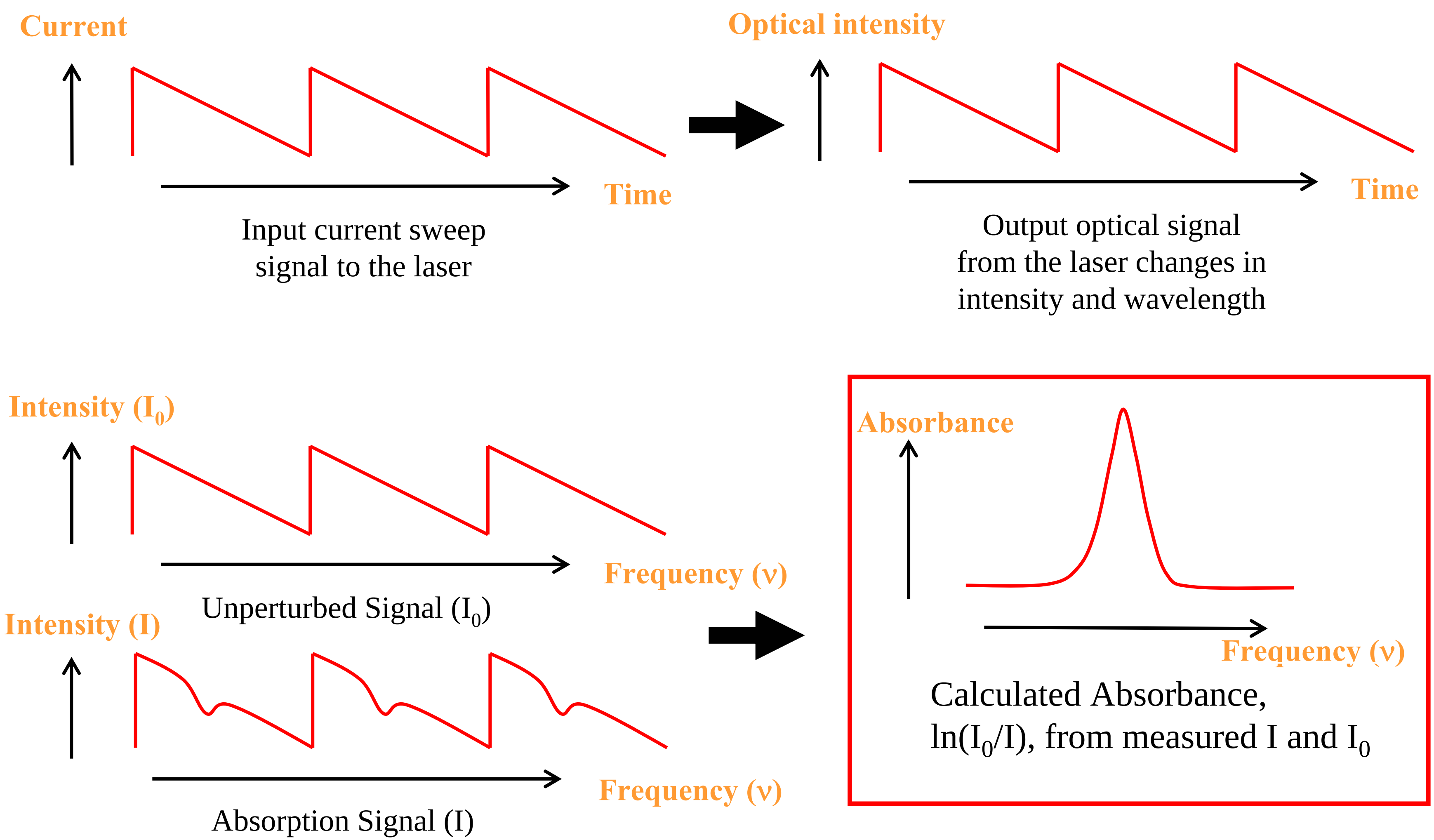
$$\frac{dI(\bar{\nu})}{I_0(\bar{\nu})} = -k(\bar{\nu}) \cdot C \cdot dx$$

- **Concentration measurements**
  - Integrated absorption of spectral line
  - Calibration

$$\bar{A} = \int_{line} k(\bar{\nu}) C L d\bar{\nu} = \bar{k} C L$$

$$C_{sample} = \frac{\bar{A}_{sample}}{\bar{A}_{calibration}} \cdot C_{calibration} \cdot r_{path}$$

Theory of absorption spectroscopy



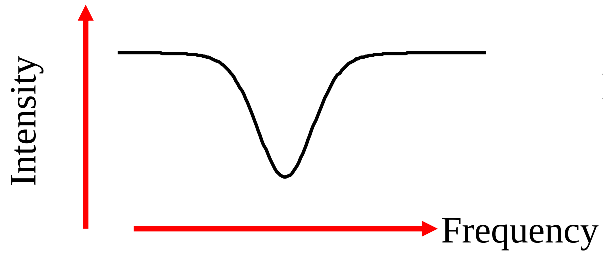
Key: Wavelength Modulation Spectroscopy (WMS)

Problem: difficulty in detecting a small dip in a large signal, particularly with a fluctuating background

- **Attributes of WMS**
  - Increases sensitivity by 2-3 orders of magnitude
  - Eliminates most flow-related sources of noise
  - Allows frequency-domain multiplexing and demodulation

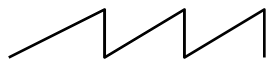
Direct absorption vs. "Wavelength modulation"

Typical absorption line shape



Function of collisional and Doppler broadening (Lorentzian shape) + (Gaussian shape)

Direct absorption



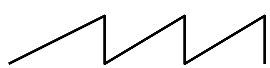
50 - 1000 Hz sweep of laser current

$$I / I_0 = \exp(- S_T g(\nu - \nu_0)\, L P_{abs})$$

Beer's law absorption

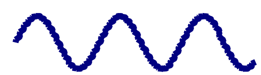
Problem: measurement of small signal on large background

Wavelength modulation



50 - 1000 Hz sweep of laser current

+



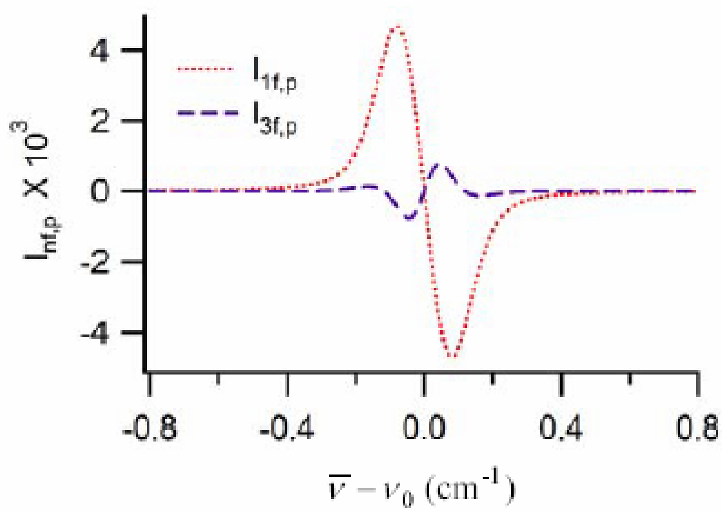
kHz rates modulation

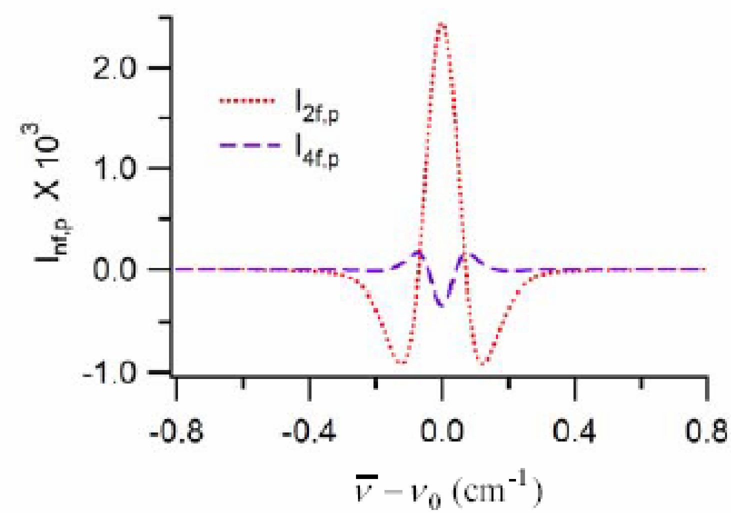
- Modulation rejects flow-related noise, electrical noise, etc., typically 1/*f*
- Detection of 1*f*, 2*f*, etc. signals with lock-in amplifier

How WMS works

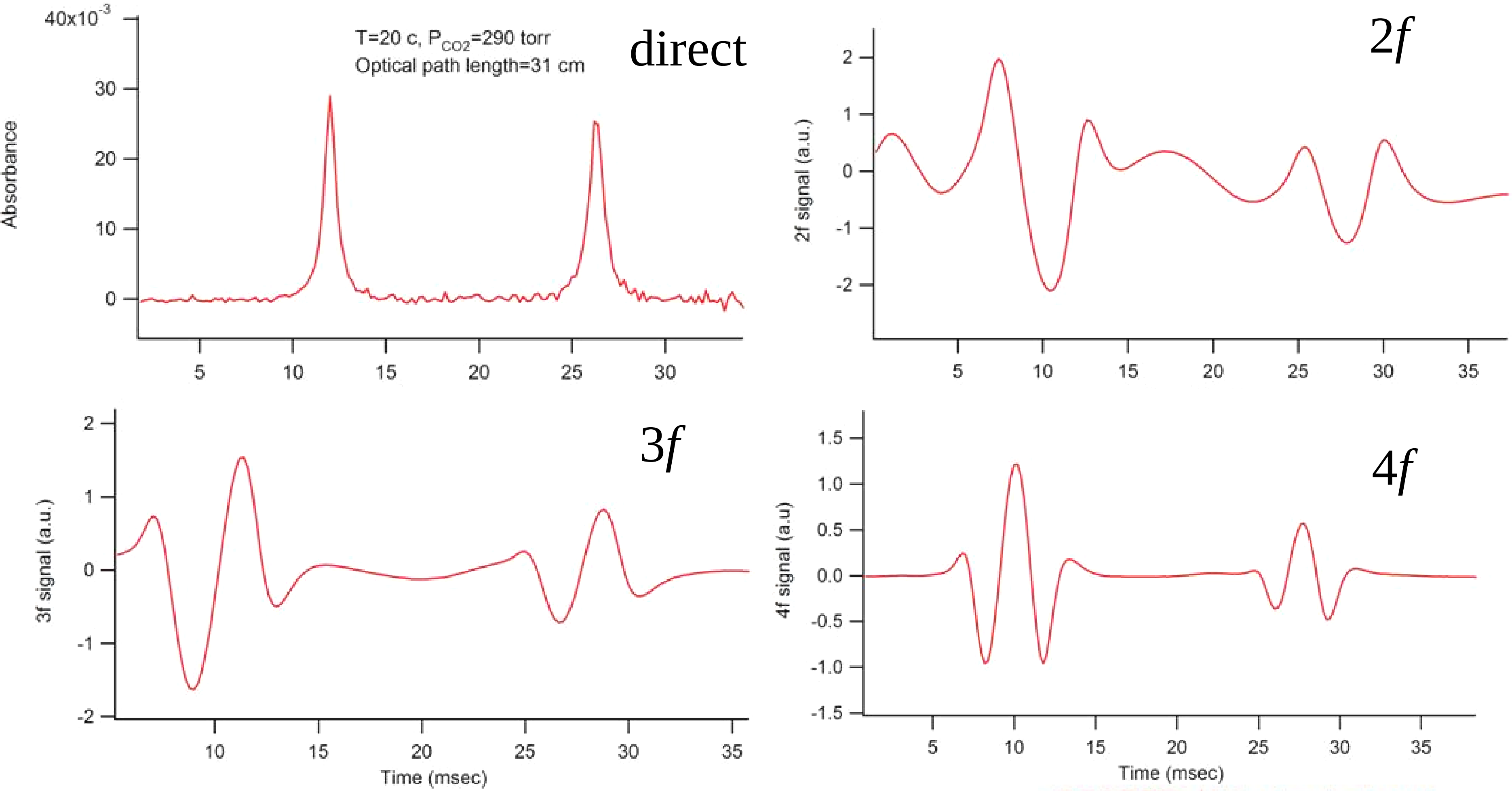
Generate driver signal → Laser controller modulates laser drive current → Laser frequency is modulated → Light is absorbed → Detector catches light → A lock-in amplifier compares detected signal with driver signal

- **Harmonic signals look like derivatives of the absorption line, hence sometimes called “derivative spectroscopy”**





Comparison of direct absorption, 2f, 3f, and 4f signals of 200 torr CO_2



How is the signal processed?

$$I_{2f} = I_0 \cdot H_2(\nu - \nu_0) \cdot S_T \cdot g(\nu - \nu_0) \cdot L \cdot P_{abs}$$

Measured signal

Initial intensity

Fourier coefficient (known function of amplitude of modulation and line width)

Absorption coefficient has two parts – a temperature-dependent line strength S_T, and a line shape function g

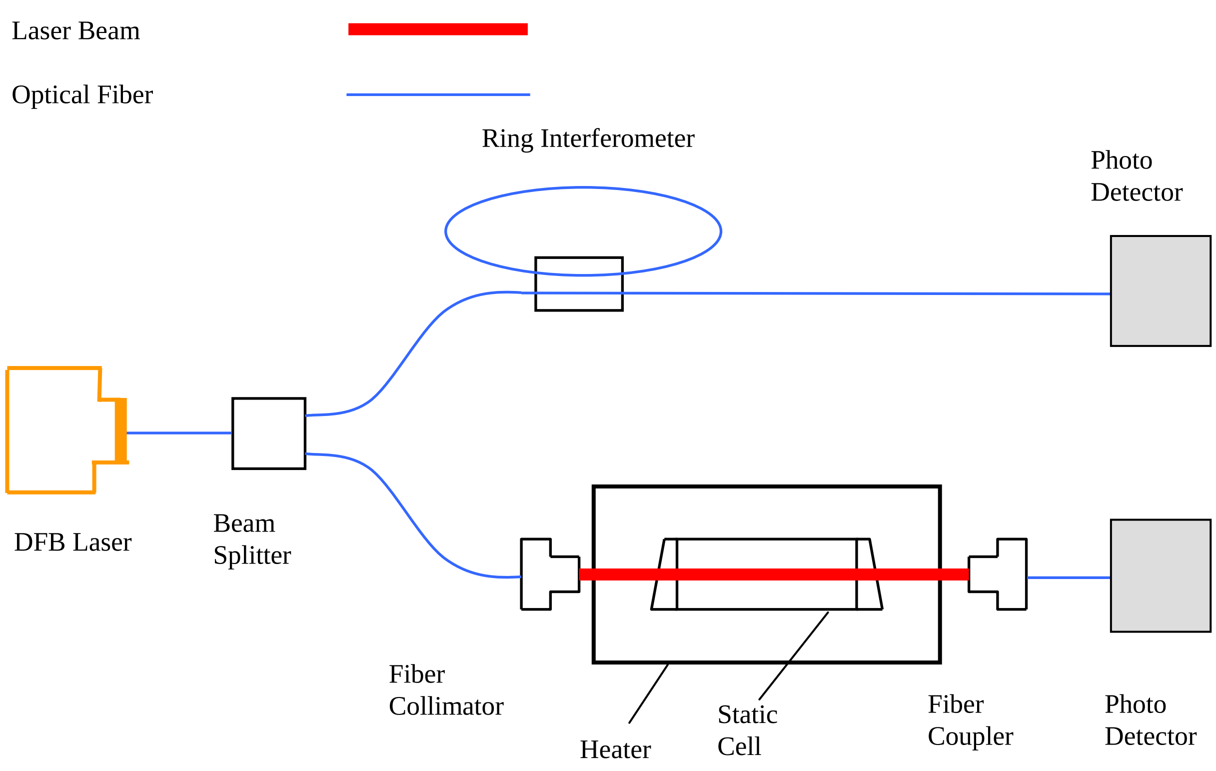
Path length (known)

Pressure of the absorbing species – what we want to find out

Line strength and line shape are functions of T and P, must be known to quantify WMS signal…

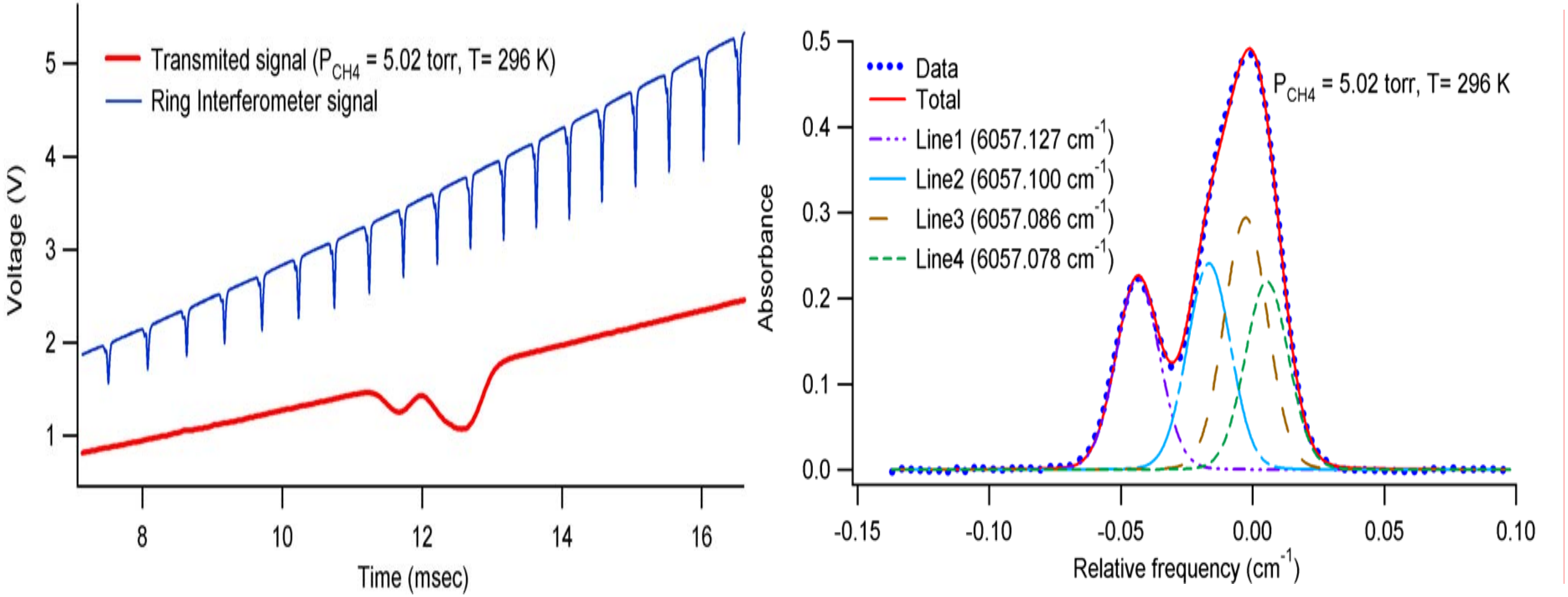
Experiments measure the temperature and pressure broadening characteristics of each absorption line

- **Schematic of the experimental apparatus for line strength and pressure broadening measurements (at different temperatures) is shown below**



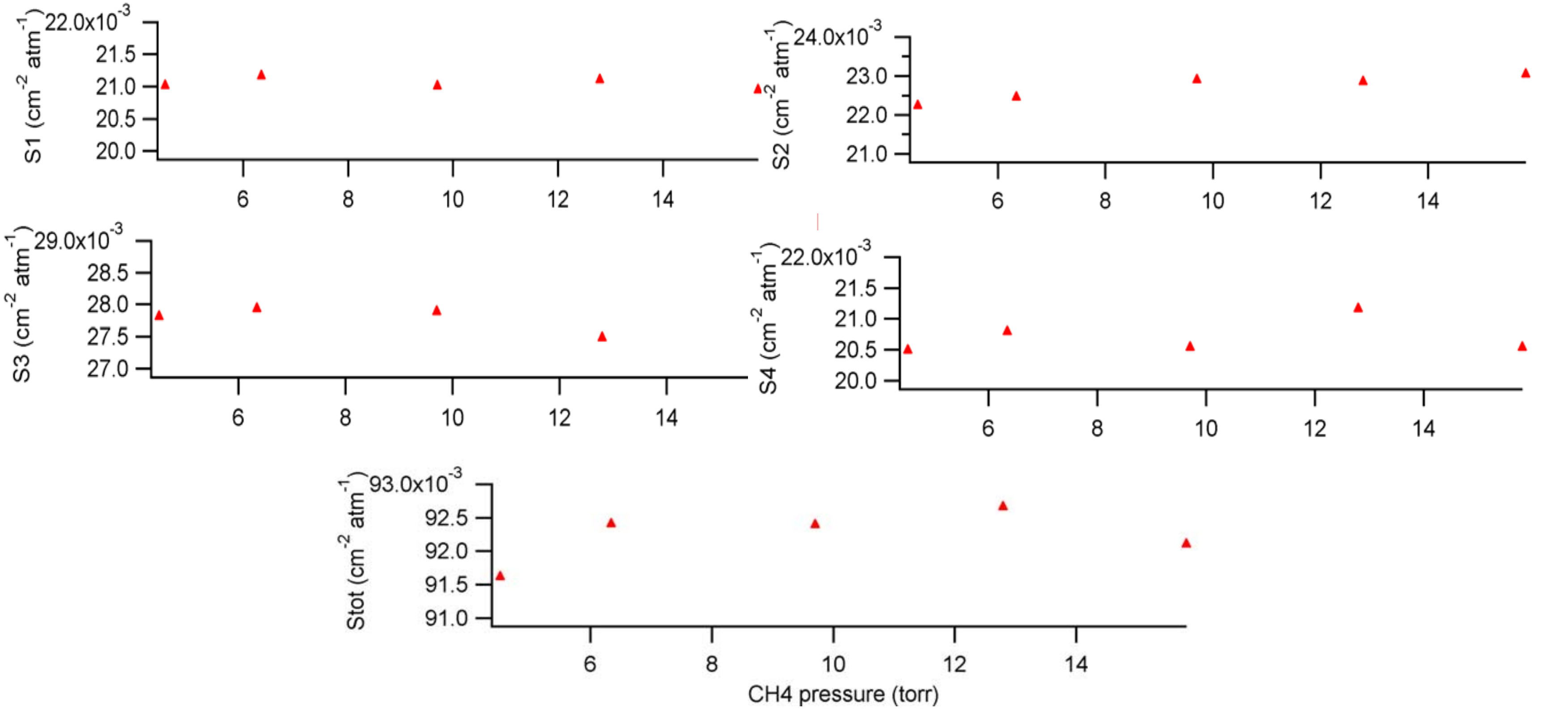
Example: Line strength measurements as a function of temperature

- **Measurements of R(4) CH_4 transition are fit to model to derive line strengths as a function of temperature**



Example: Line strength measurements as a function of temperature

- Measured individual line strengths of CH_4 R(4) manifold at T=296 K (Should be pressure-independent)



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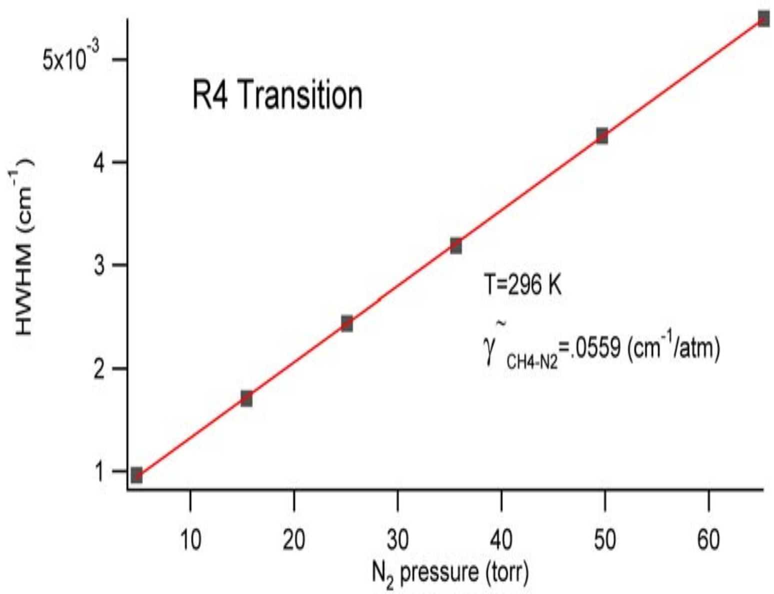
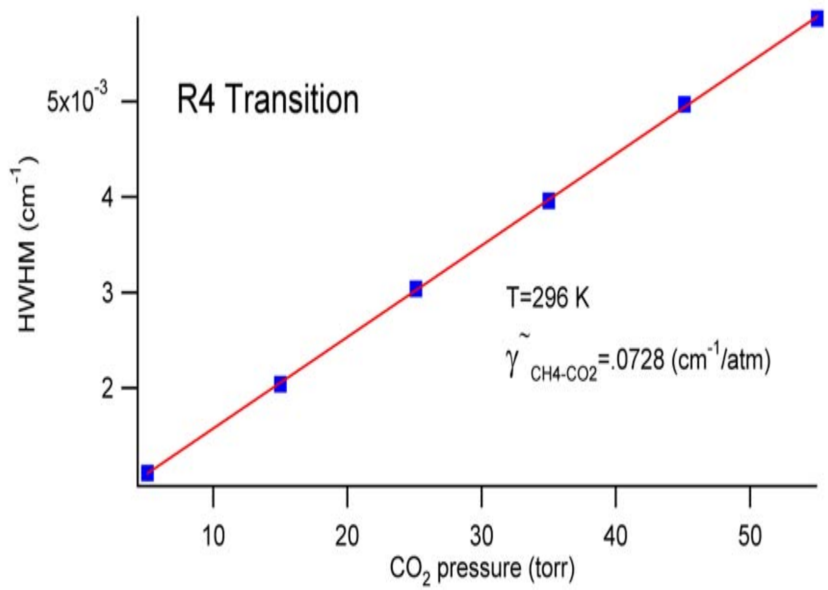
Example: Pressure broadening measurement for CH_4 transitions

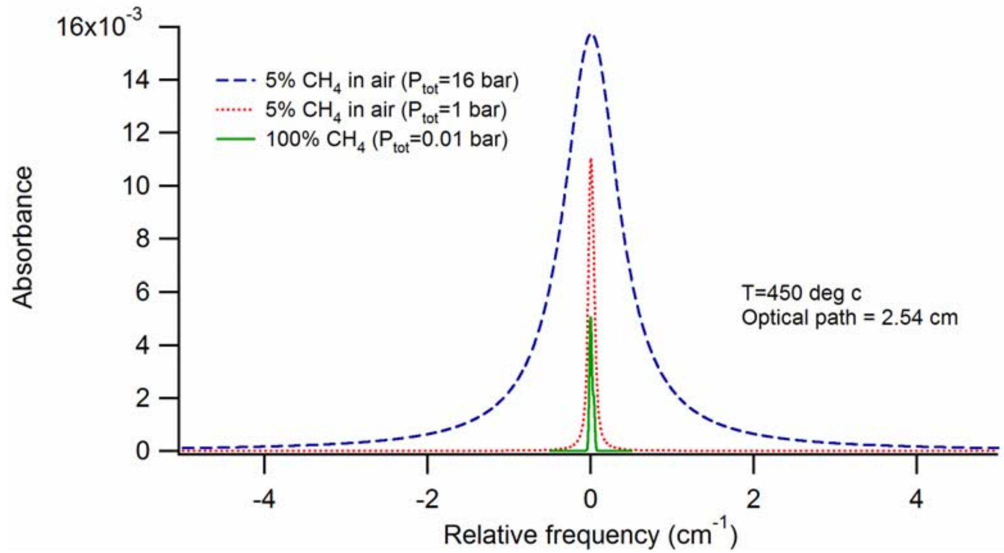
- **Each gas component in the mixture contributes independently to line broadening – must be measured**





WMS at high pressure: Line-locked measurements

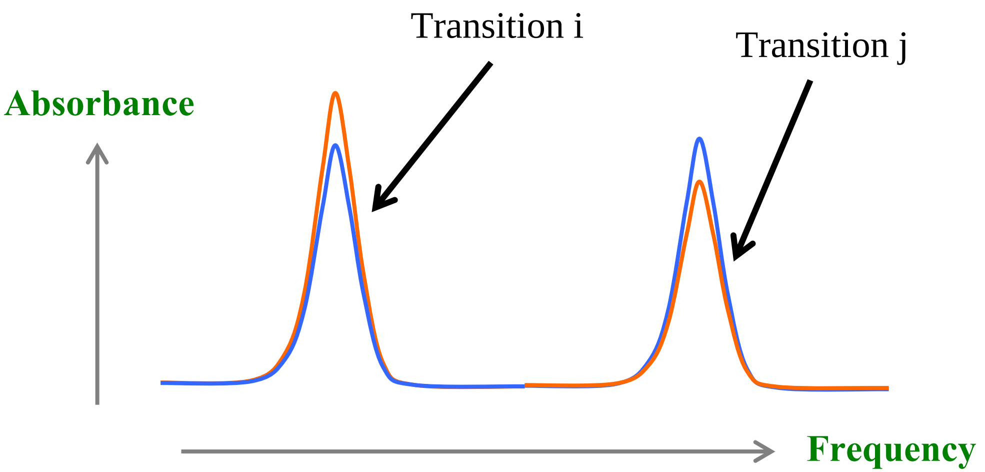
- **Increased broadening dramatically increases line width at high pressures**
- **Most near-infrared TDLs only tune 1-2 cm^{-1}**



- **Solution – eliminate the "sweep" signal, only modulate the laser about the line center**

➔ Relies on having very accurate models of the line for interpretation of the signal

TDL-based temperature measurements

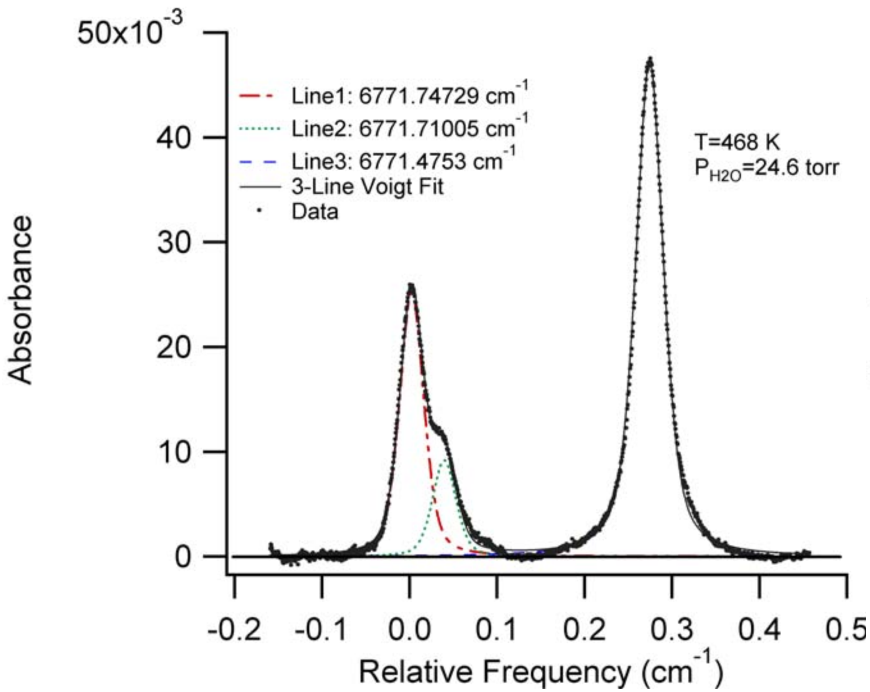


Schematic variation of line strength of two absorption lines with temperature

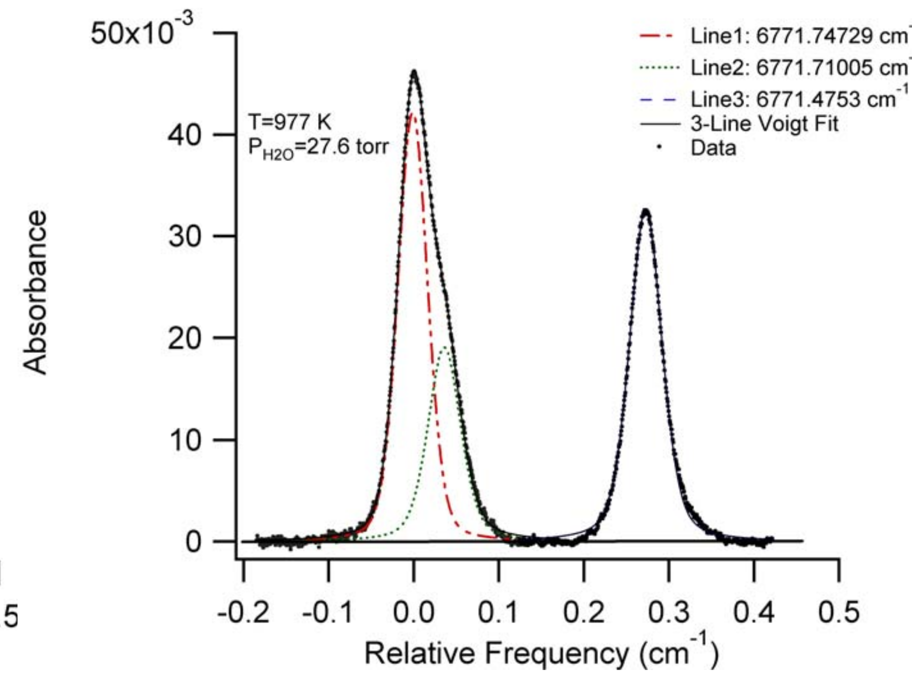
$$R_{abs}(T) = \frac{S_i(T)}{S_j(T)}$$

TDL H_2O / Temperature measurement

Measured absorbance of selected H_2O transitions (near 1478 nm) at two different temperatures



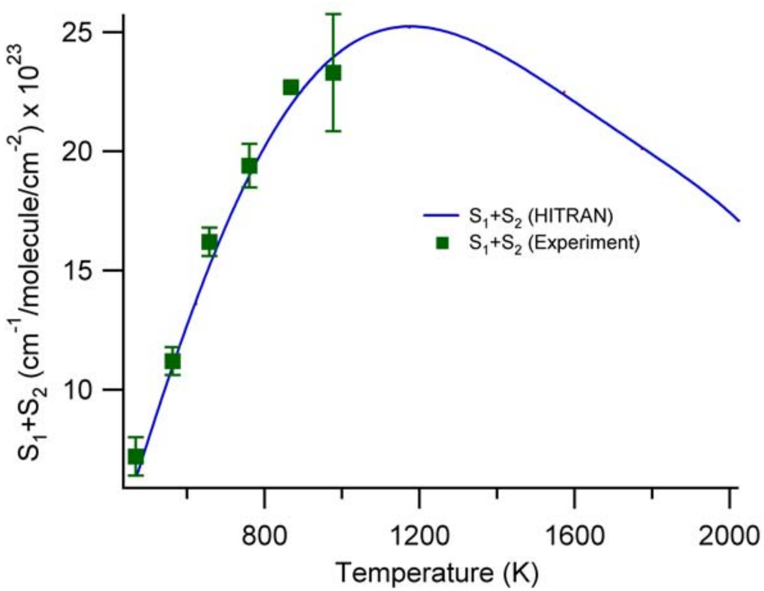
At T1=468 K

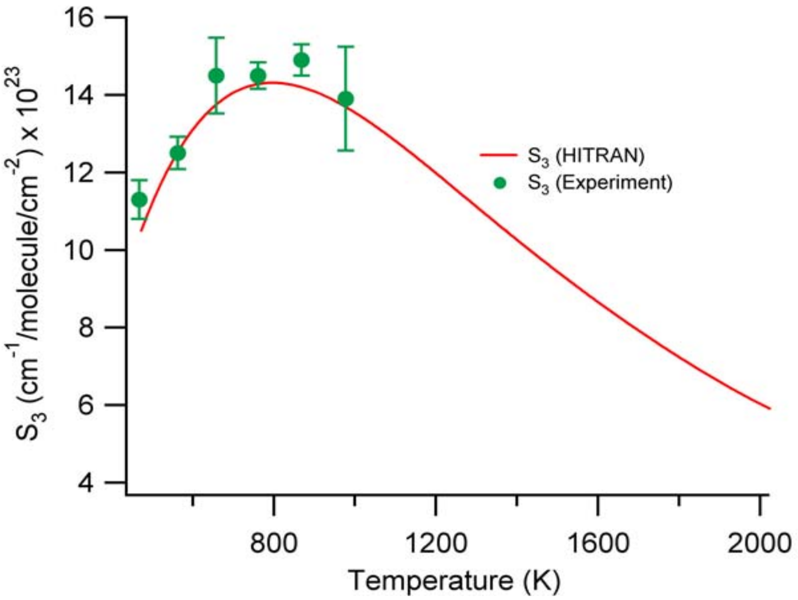


At T2=997 K

TDL H_2O / Temperature measurement

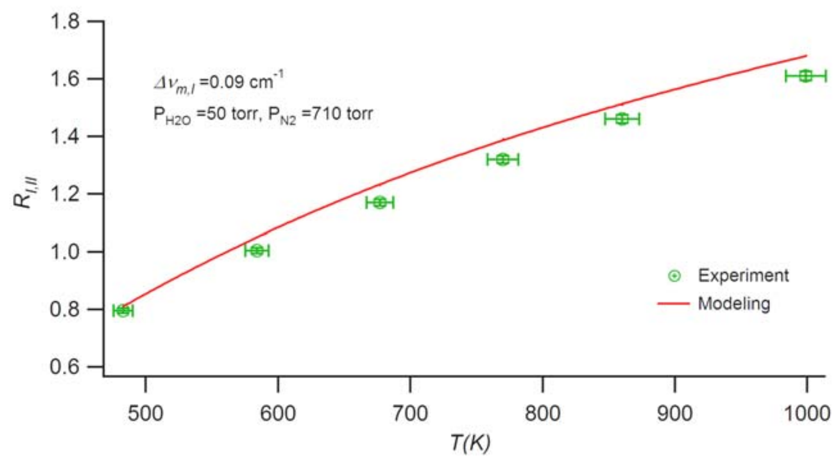
Measured absorption line strengths of the selected H_2O transitions vs. temperature

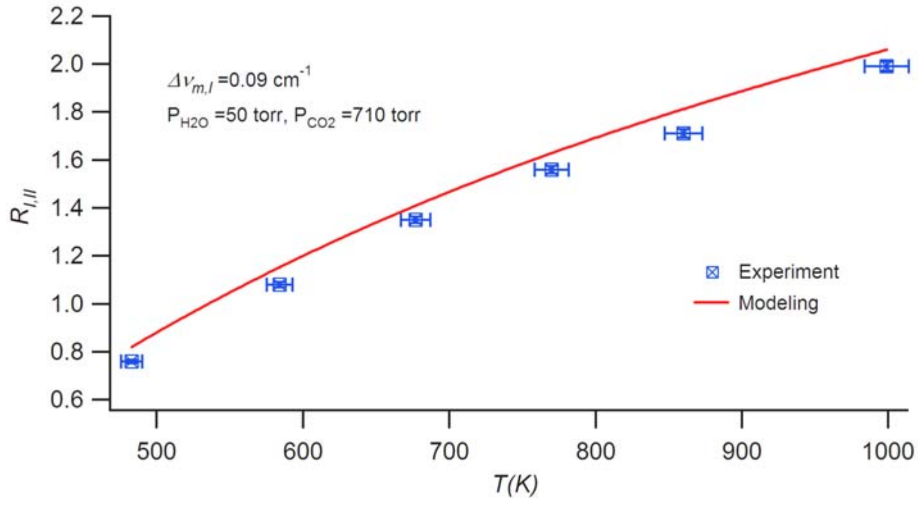




TDL H_2O / Temperature measurement

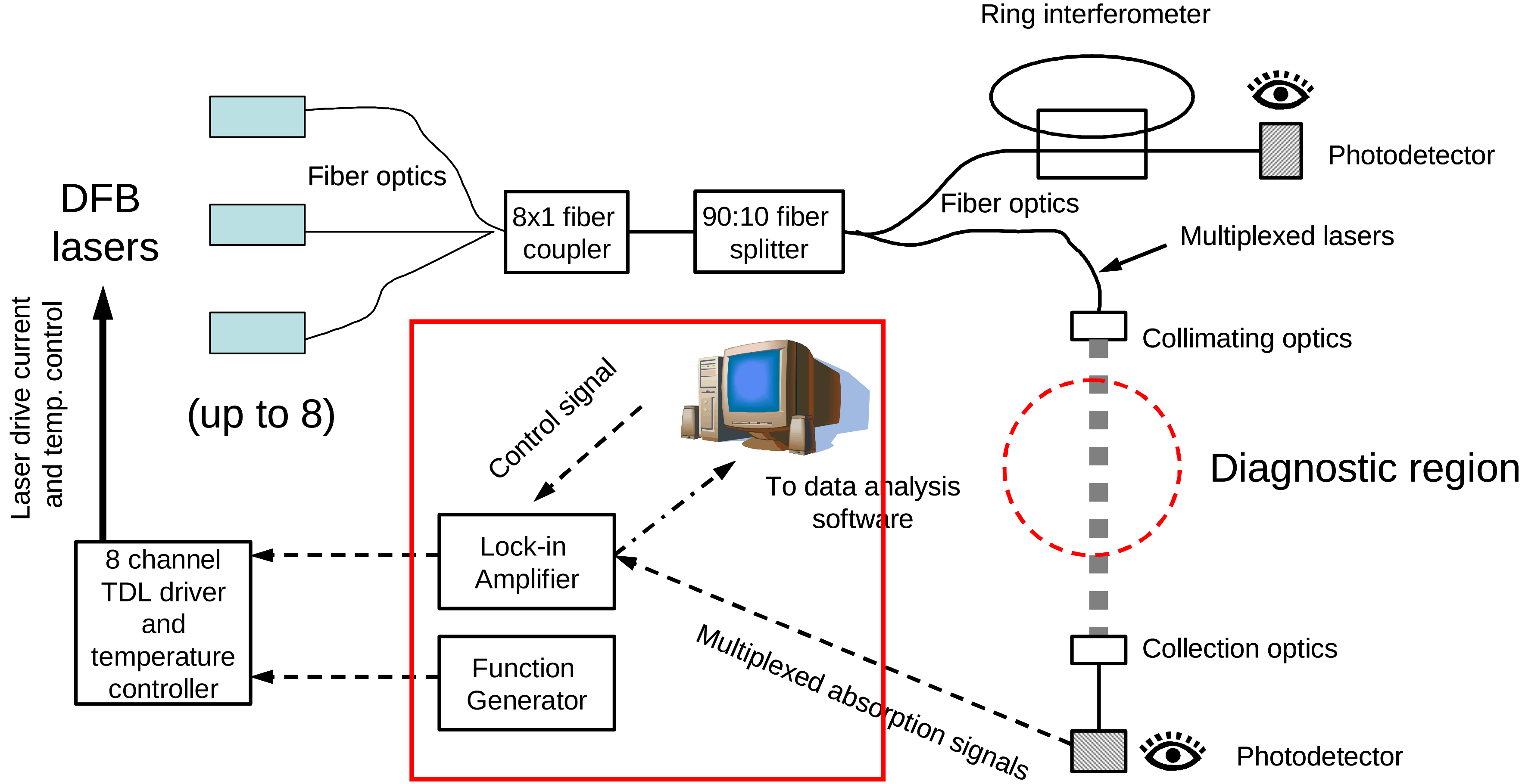
Variation of absorption ratio vs. temperature





- **Accurate models of spectral lines are crucial for variable conditions**

Overall sensor architecture

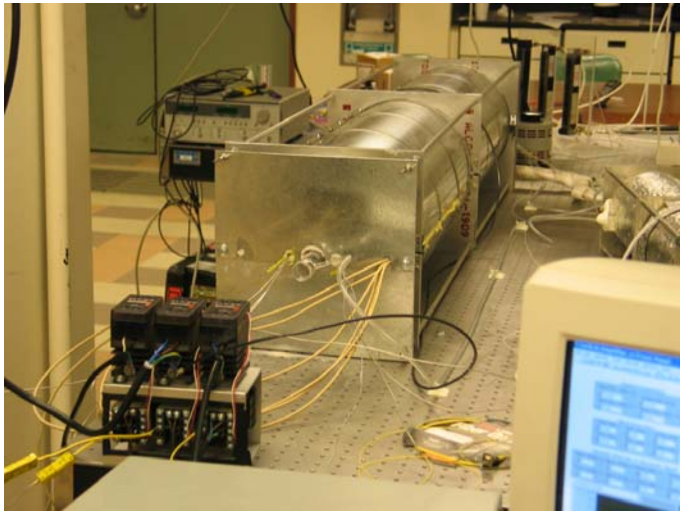


All accomplished in Labview™

Progress to date in sensor development

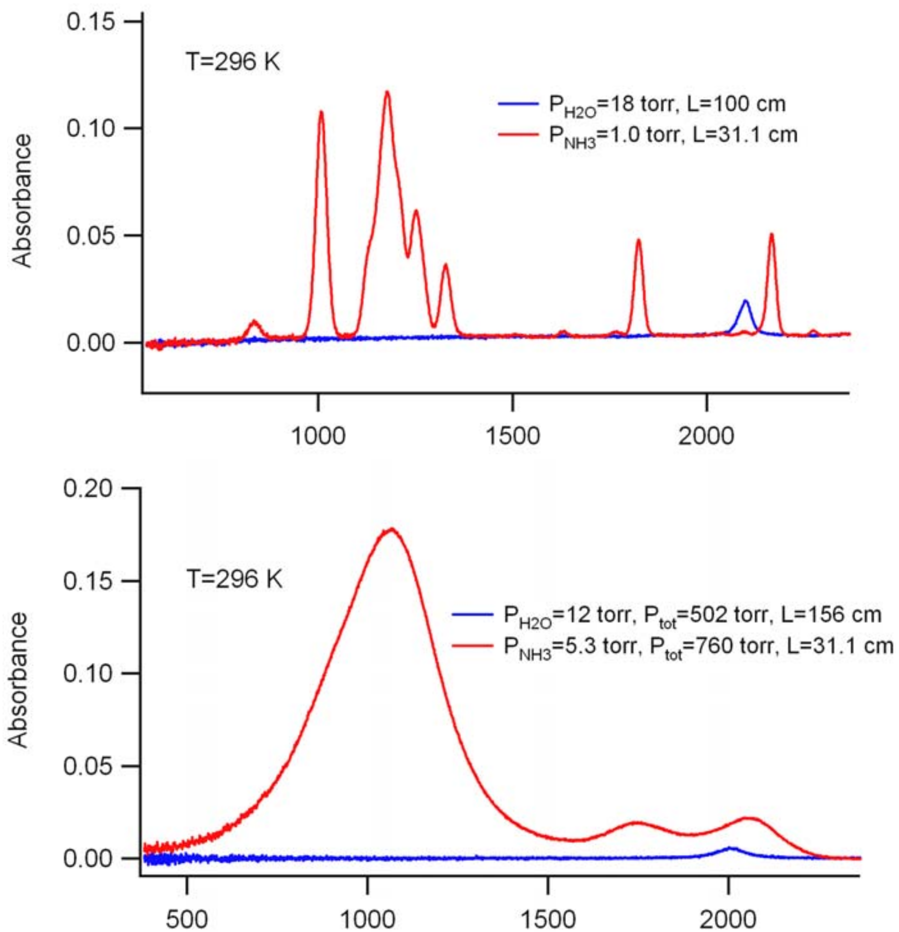
- **H_2O, CH_4, CO, and CO_2 spectroscopy are completed**
  - A new long-pathlength, high-pressure cell was constructed for these measurements
  - We have complete pressure broadening and temperature data for these species
- **NH_3 and H_2S are in progress**
  - Lasers have been received, lines have been selected
  - Initial spectra have been acquired, characterization of pressure broadening and temperature data is proceeding
  - Difficulty with toxicity of species, and complexity of spectra
    - A cell and flow system for these toxic gases has been constructed

Completed hardware



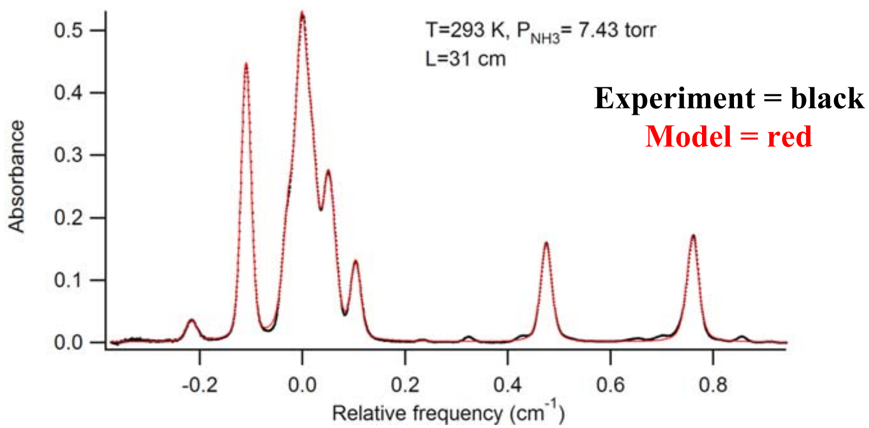
- Long path, high-temperature cell allows more sensitive measurements
- High-pressure cell (not shown) is used to investigate agreement of model and experiment at high pressure
- Electronics box controls multiple lasers

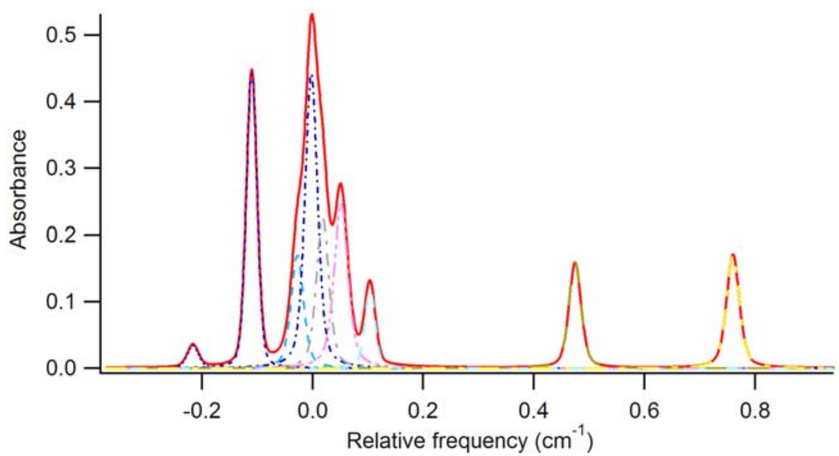
“Difficult” ammonia spectra measured in the lab



- **Very complicated**
  - Many peaks
  - Databases are incomplete / incorrect
- **In the lab, cannot test at high temperature with H_2O present**
  - Constructed multiple-path experiment
- **Top = low pressure, Bottom = atmospheric pressure**

We have constructed a model for NH_3 spectra





- Upper trace → total spectra, predicted versus modeled
- Lower trace → individual modeled lines
- For quantification, it was necessary to model 21 individual lines
- Model particularly useful for pressure-broadened measurements
- Time-consuming to construct
- Similar effort underway for H_2S

Progress to date: Design and construction

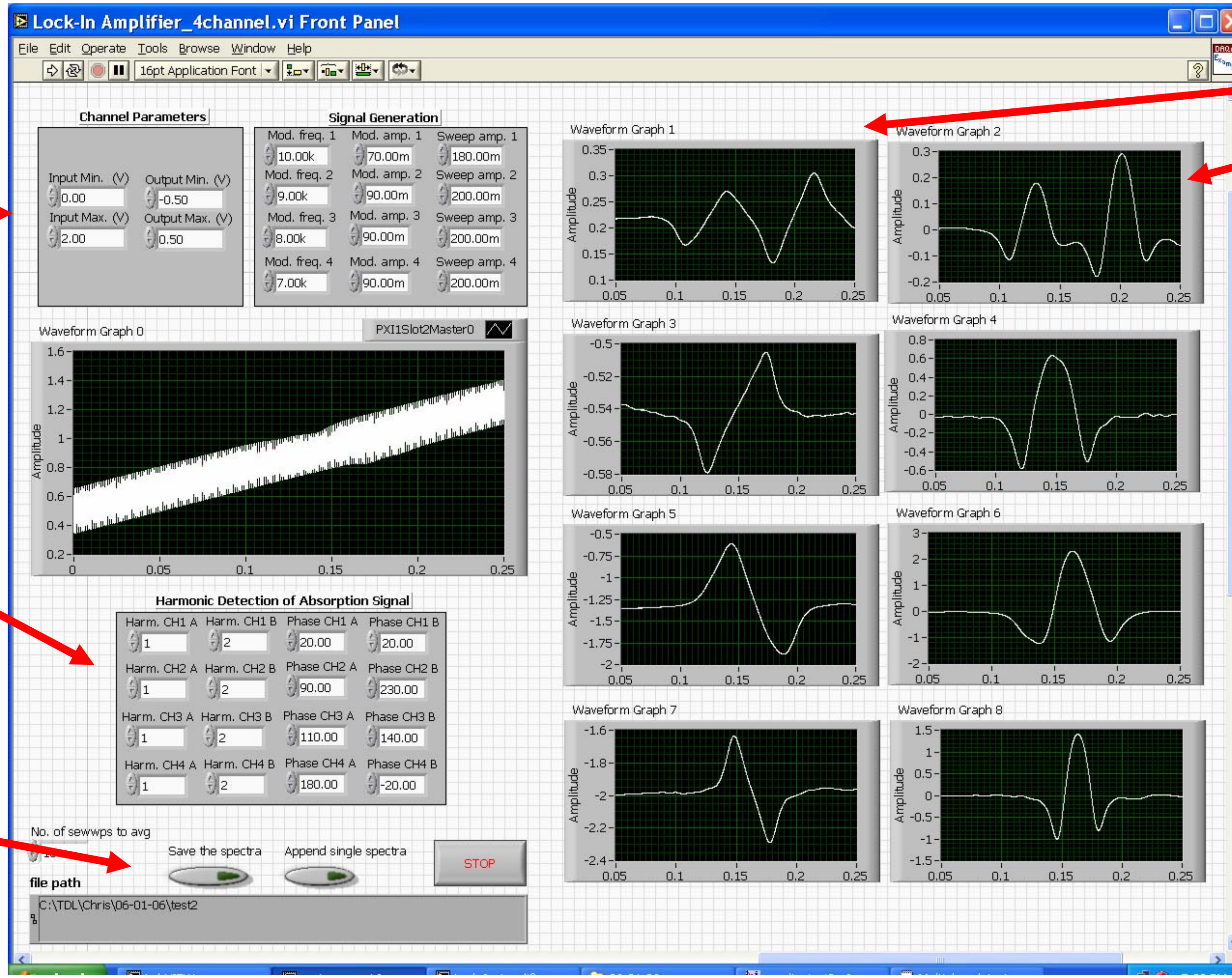
- **National Instruments' PXI system and ILX Lightwave temperature controller / diode driver have been integrated into system**
- **Two electronics boxes have been designed, built, and tested**
  - a modulation box that takes a single sweep input and superimposes 4 modulation signals of fixed frequency and variable amplitude
  - a reference box that normalizes the detector signal by the input laser power to correct for fluctuations and nonlinearities in the laser signal
- **Hardware is essentially in final form**

Advanced Labview™ software built and tested

Control of laser parameters

Control of graphical output

Ability to save spectra

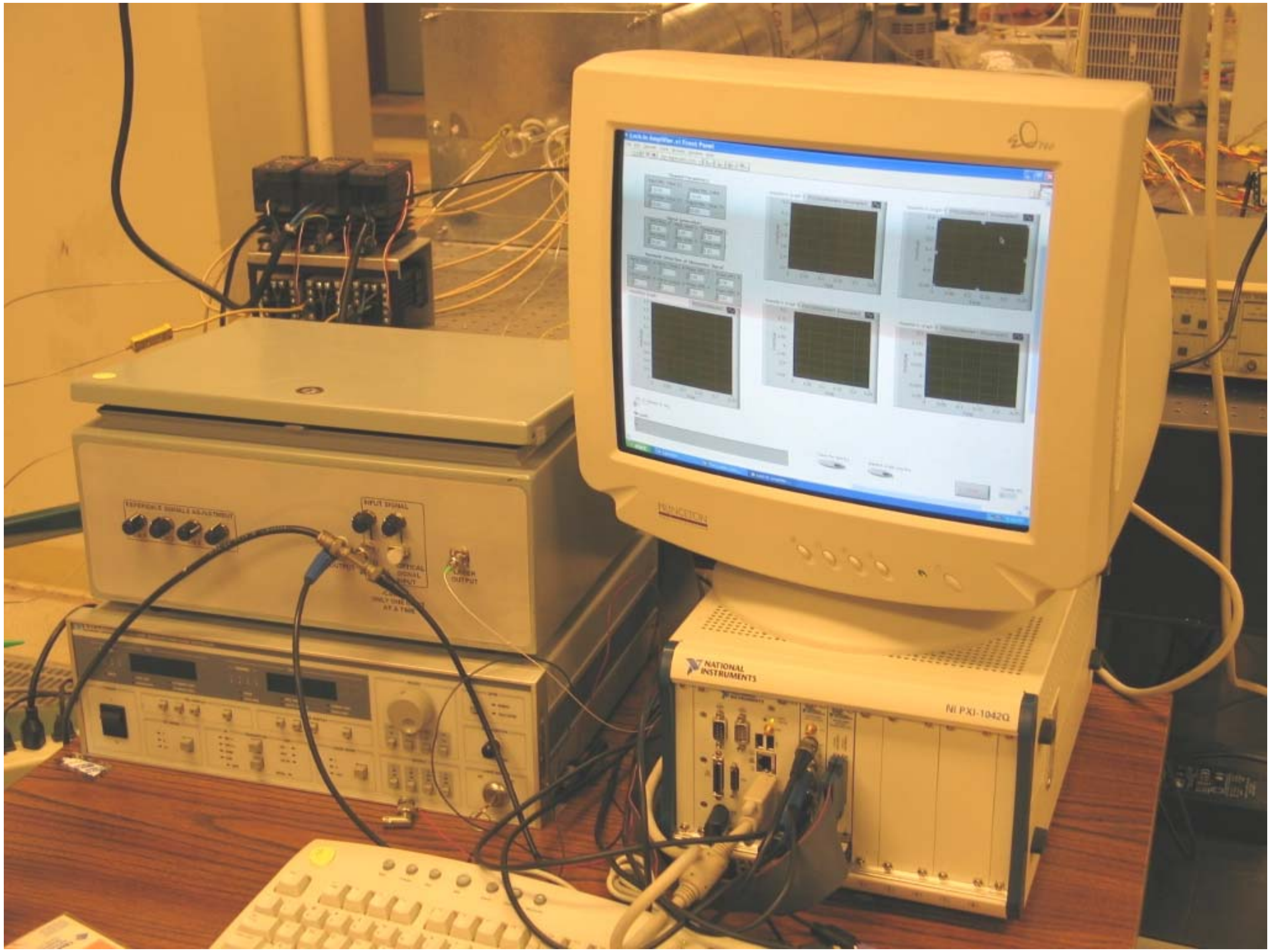


1st harmonic (column)

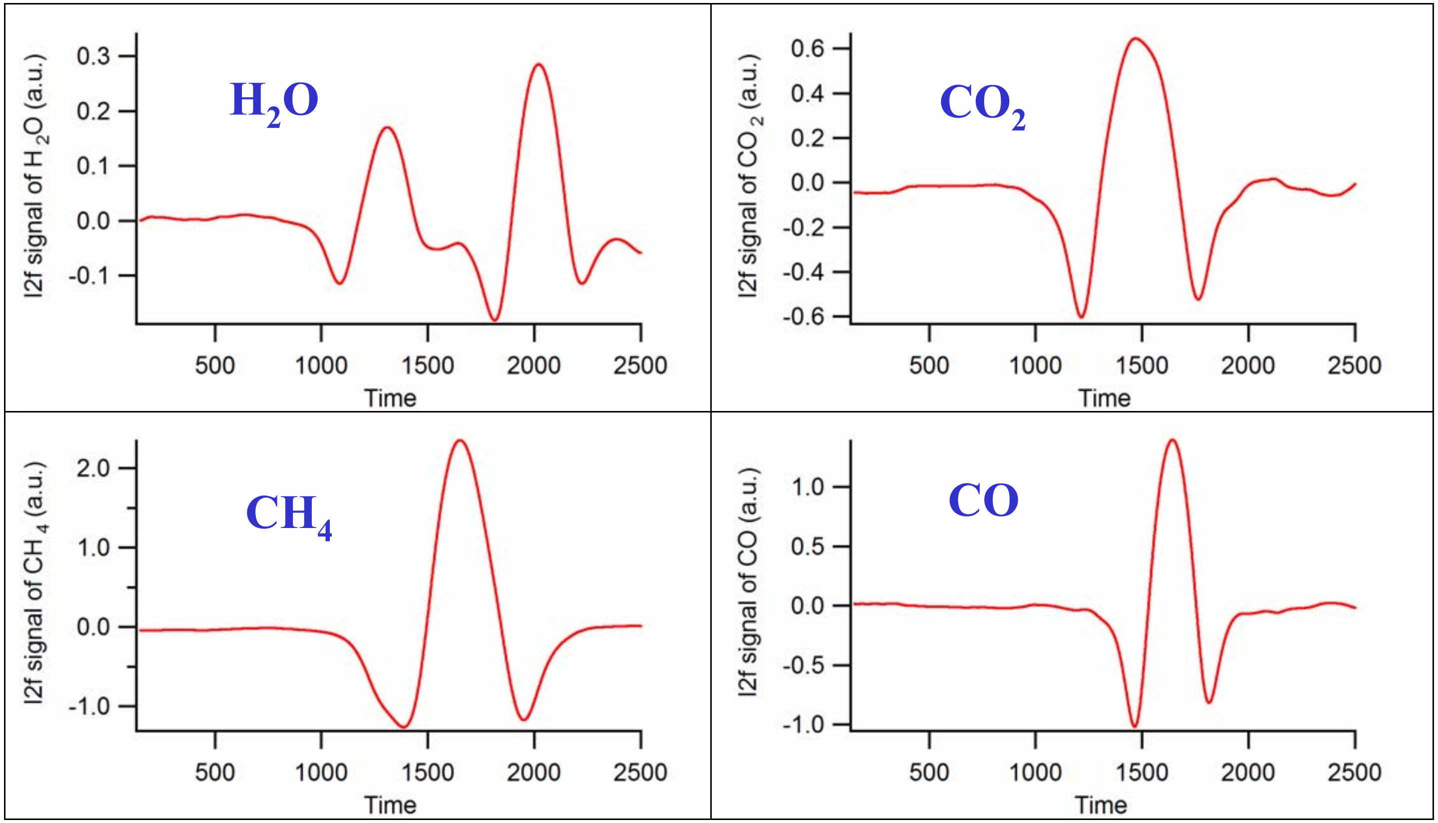
2nd harmonic (column)

Four channels showing H_2O, CO_2, CH_4, and CO spectra

Entire assembly in the lab

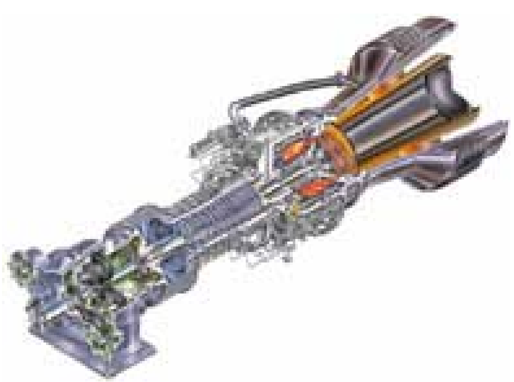


System allows simultaneous recording of multiple real-time spectra on a single detector



Field Trials: September 2005 and April, 2006

- The UCSD campus (~23,000 students, 1,200 acres) generates most of its own power using 2 Solar Turbines Titan 130, 13 MW gas turbines
- Internal funding supported real-time measurements on the turbines for emissions monitoring and oscillation detection
- CO_2, H_2O, and temperature were monitored



Key results

➔ Each of these was a "projected milestone" last year

- **H_2O, temperature, CO, CO_2 and CH_4 have been simultaneously measured and quantified at high temperature using collisional broadening and line strengths measured in the laboratory**
- **NH_3 and H_2S spectra have been obtained, measurements of parameters and modeling are both proceeding**
- **Architecture is finished and tested**
- **Labview™ lock-in program coupled with data acquisition system has been successfully tested**
- **On-campus field trials have been helpful to eliminate errors in system and improve software**

Upcoming milestones

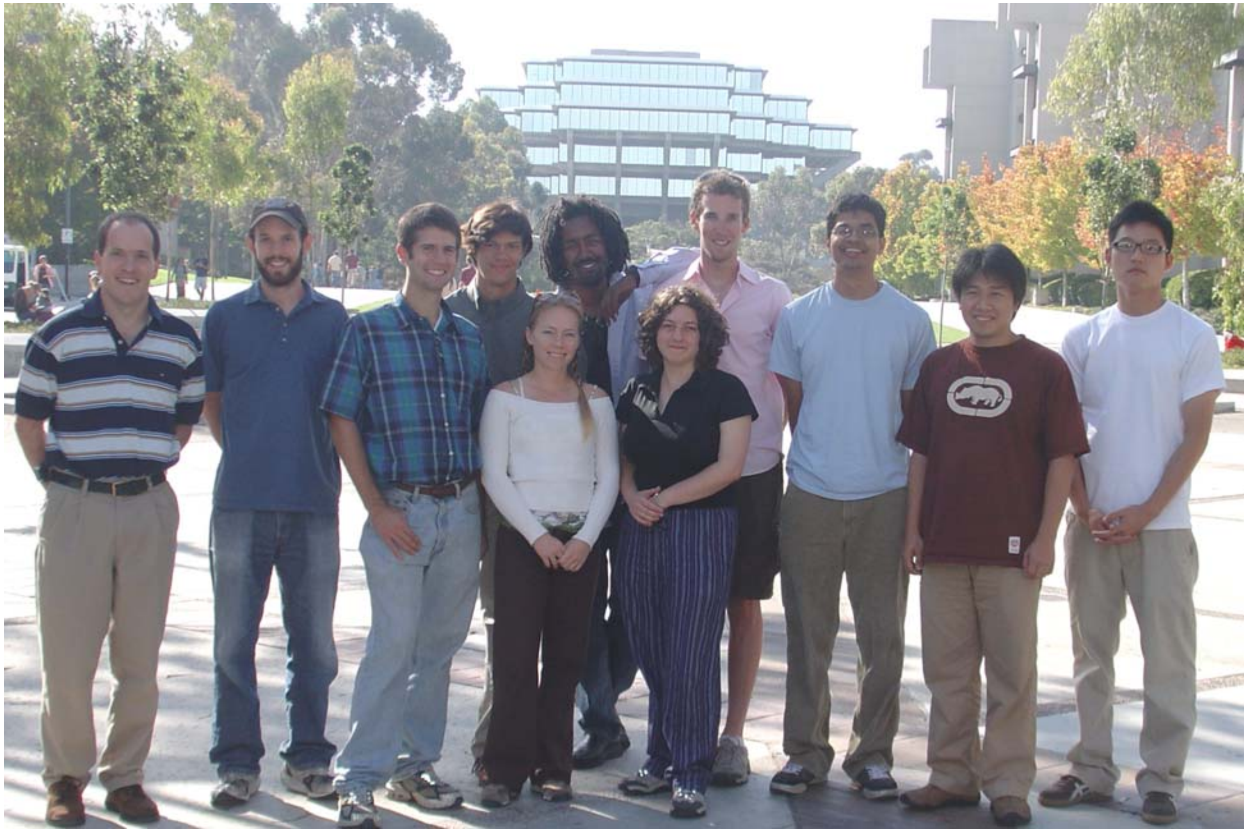
- **Finish NH_3 and H_2S spectroscopy**
- **Add calibration to software so that reporting can be in "real units"**
- **Final – measurements on an operating gasifier**

Summary and Conclusions

- **Project is making substantial progress with respect to research and development goals**
- **Hardware development and spectroscopy development have been mostly completed**
  - CH_4, H_2O, CO, CO_2 spectroscopy all finished
  - Labview™ software replaced substantial hardware, adds versatility
  - Extra time was required for NH_3 and H_2S, beyond proposal estimates
- **Second field trial appears to have been successful**
  - Quantification in process
  - Calibration will be incorporated into softrware
- **Final goal: test on an operating gasifier**
  - Have been in touch with Dr. Tom Gale at the Southern Company gasifier about the potential for measurements there

Selected recent and in-preparation papers

- M. Gharavi and S.G. Buckley, "Diode Laser Absorption Spectroscopy Measurement of Line Strengths and Pressure Broadening Coefficients of the Methane $2\nu_3$ Band at Elevated Temperatures," *Journal of Molecular Spectroscopy* 229 pp 78-88 (2005).
- M. Gharavi and S.G. Buckley, "Near-infrared optical sensor for monitoring NH_3," to be presented, FACSS 2006.
- M. Gharavi and S.G. Buckley, "Pressure broadening parameters of H_2O absorption transitions of $2\nu_1$ and $2\nu_2+\nu_3$ bands at elevated temperatures," *submitted, Journal of Quantitative Spectroscopy & Radiative Transfer*.
- M. Gharavi and S.G. Buckley, "Wavelength modulation spectroscopy for temperature and H_2O concentration measurement using a single diode laser," *submitted, Applied Optics*.
- M. Gharavi, M. Leon, and S.G. Buckley, "Real-Time Measurement of H_2O, CO, and Temperature in an Operating Gas Turbine," to be submitted to *Measurement Science and Technology*.
- A. Schuger, M. Gharavi, and S.G. Buckley, "In-Flame, Real-Time Measurement of H_2O, CO, OH, and Temperature," to be submitted to *Combustion Science and Technology*.
- M. Gharavi, C. Lao, and S.G. Buckley, "Line Strengths and Pressure Broadening of Selected Transitions of CO and CO_2," to be submitted to *Journal of Molecular Spectrosocpy*.



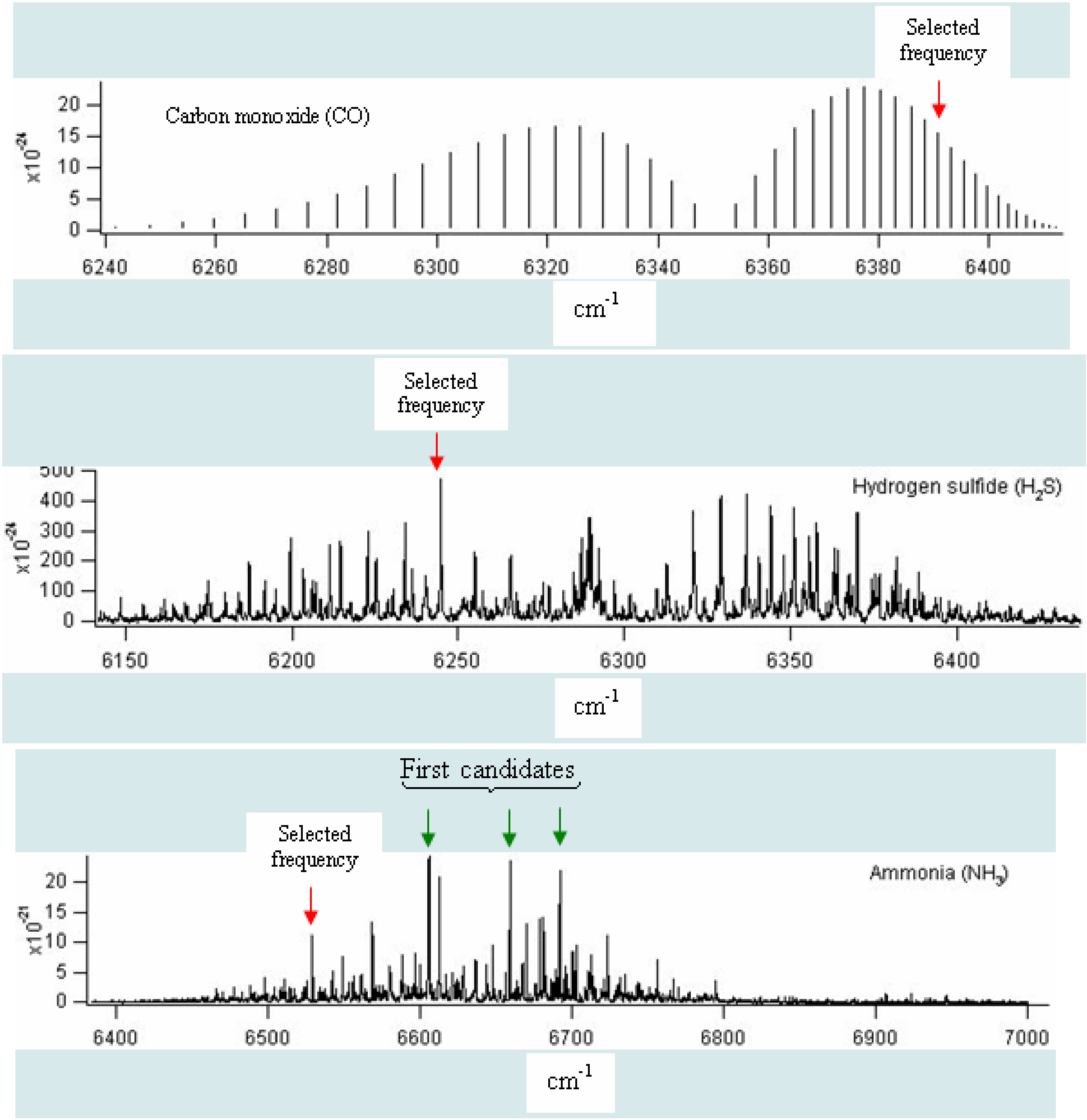
Thanks for your attention!

We appreciate the kind assistance of our program manager Robie Lewis and the support of DOE on this project

Additional slides

National Instruments data acquisition system

- PXI system has integrated Windows™-based microprocessor, 6 channels of 500 kHz analog input and 2 channels of analog output
- Completely configurable using Labview™ graphical programming language designed for data acquisition
- Enough horsepower to do some real-time computations
- Rugged and portable



Laser selection

- Modeled and experimental spectra are consulted to find best lines in near infrared
- Lines are checked for interferences from H_2O and other gases
- Laser manufacturers are contacted to determine laser availability